



Sensitivity to friction for primary explosives

Robert Matyáš*, Jakub Šelešovský, Tomáš Musil

Institute of Energetic Materials, Faculty of Chemical Technology, University of Pardubice, Pardubice 532 10, Czech Republic

ARTICLE INFO

Article history:

Received 26 September 2011
Received in revised form 24 January 2012
Accepted 26 January 2012
Available online 3 February 2012

Keywords:

Primary explosives
Sensitivity
Sensitivity to friction

ABSTRACT

The sensitivity to friction for a selection of primary explosives has been studied using a small BAM friction apparatus. The probit analysis was used for the construction of a sensitivity curve for each primary explosive tested. Two groups of primary explosives were chosen for measurement (a) the most commonly used industrially produced primary explosives (e.g. lead azide, tetrazene, dinol, lead styphnate) and (b) the most produced improvised primary explosives (e.g. triacetone triperoxide, hexamethylenetriperoxide diamine, mercury fulminate, acetylides of heavy metals). A knowledge of friction sensitivity is very important for determining manipulation safety for primary explosives. All the primary explosives tested were carefully characterised (synthesis procedure, shape and size of crystals). The sensitivity curves obtained represent a unique set of data, which cannot be found anywhere else in the available literature.

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1. Introduction

Primary explosives form a group of explosives that are considered to be highly sensitive to some mechanical stimuli such as impact, friction, stab, heat, static electricity, flame etc. Sensitivity of explosives to friction is one of the fundamental sensitivity parameters. Compounds are subjected to friction practically every time they are handled – at pouring, mixing, filling ready for application, etc. Determining sensitivity to friction is therefore very important for determining manipulation safety of primary explosives.

A large number of types of apparatuses for determining friction sensitivity has been developed up to date [1]. Each apparatus is different even in its construction. Moreover there are several methods for measuring and evaluating the sensitivity data (e.g. up and down, lowest friction force, probit analysis). Therefore it is practically impossible to compare sensitivity data measured in different laboratories using different methods. A frequent drawback to many papers dealing with explosives' sensitivity to mechanical stimuli is the lack of sufficient description of samples measured (mainly size and shape of crystal plus preparation procedure). These parameters have a significant impact on the sensitivity to mechanical stimuli. E.g. the dependence of impact sensitivity on crystal size in case of a primary explosive (lead azide) was first described by Bowden and Singh in 1953 [2].

Friction sensitivity is usually published only as an additional characteristic in a paper dealing with the particular primary explosive, with the better case being when the value is compared to a

standard (lead azide, mercury fulminate or lead styphnate). The comparison of two values from two different articles is almost impossible (due to the different apparatus and different methods used).

We found very few papers containing friction sensitivity data for several primary explosives or dealing with comparison of sensitivity of primary explosives among themselves. The earliest paper that we found was published by Taylor and Rinckenbach in 1927 [3], who published sensitivity data for several primary explosives. The authors have also well described preparation procedures and the description of samples measured. Wallbaum published sensitivity curves for 7 industrially used primary explosives in 1939 [4]. Le Roux published an extensive study of the impact of rubbing surface roughness on sensitivity of several industrial primary explosives in 1990 [5]. Nowadays, the Meyers handbook "Explosives" is a frequently used source of sensitivity data for various explosives. However this book contains only one value (the smallest load of the peg at least once in six consecutive trials) for each primary explosive [6]. Therefore we carried out an extensive study of two important groups of primary explosives:

1. industrially used and produced;
2. improvised primary explosives.

A knowledge of friction sensitivity of both groups is very important for safe handling of primary explosives in the production process and subsequent handling (industrial primary explosives) or during its disposal by EOD (improvised primary explosives).

We decided to compare the friction sensitivities of 14 primary explosives (including both industrial and improvised) due to the lack of such data in the available literature. The friction sensitivity

* Corresponding author. Tel.: +420 466038018; fax: +420 466038024.
E-mail address: robert.matyas@upce.cz (R. Matyáš).

curves of all samples have been measured using a single apparatus (small scale BAM) and one measuring method (probit analysis). The whole dataset is contained in this article.

2. Experimental part

Warning – all primary explosives are very sensitive to impact, friction, electric discharge and flame. The synthesis and handling of them are dangerous operations that require standard safety precautions for handling primary explosives!

2.1. Synthesis of primary explosives

2.1.1. Silver acetylide

Silver acetylide (Ag_2C_2) was prepared according to the Stettbacher procedure [7]. Silver nitrate (2.5 g, 14.7 mmol) was dissolved in 20 ml water; then 20 ml of 25% aqueous ammonia was added to the silver nitrate solution. A solid white precipitate was formed in the reaction mixture which subsequently dissolved. Gaseous acetylene purified by passing it through four gas-washing bottles (the first contained dilute sulfuric acid; the second contained aqueous potassium permanganate mixed with sulfuric acid; the third contained a neutral solution of potassium permanganate and the last one pure water) was passed through the reaction mixture. The precipitate of silver acetylide was formed during the passing of acetylene and it settled on the bottom. The white precipitate quickly turning gray was filtered, washed up to neutral pH with water and dried at laboratory temperature. The product probably forms an amorphous substance (crystalline structure was not observed in the product with electron microscopy with magnification up to $10\,000\times$, see Fig. 1(a)).

2.1.2. The double salt of silver acetylide and silver nitrate

The double salt of silver acetylide and silver nitrate ($\text{Ag}_2\text{C}_2 \cdot \text{AgNO}_3$) was prepared according to the Stettbacher procedure [7]. Silver nitrate (2.5 g, 14.7 mmol) was dissolved in 39 ml water; then 1 ml 65% nitric acid was added. Purified acetylene (see above; preparation of silver acetylide) was passed through the silver nitrate solution. The product formed a white flaky precipitate quickly turning gray and settling on the bottom. The precipitate was filtered, washed up to neutral pH and dried at laboratory temperature. The particle size and shape, documented by electron microscopy, are presented in Fig. 1(b).

2.1.3. Copper(I) acetylide

Copper(I) acetylide (Cu_2C_2) was prepared according to the procedure published by Špičák and Šimeček [8]. Copper(II) chloride (10 g, 74.3 mmol) was dissolved in 50 ml of water followed by addition of 5 drops of 35% hydrochloric acid and 10 g (157 mmol) of copper powder. The reaction mixture was then refluxed with copper(II) reducing to copper(I). The completion of reduction was observable by discoloration of the solution; copper(I) chloride precipitated as a white precipitate. Then, 25% aqueous ammonia was added into the reaction mixture and copper(I) chloride dissolved. Residual powdered copper was filtered off. The clear reaction solution was then bubbled with pure acetylene (acetylene was purified as described in the case of silver acetylide). The red precipitate of copper(I) acetylide was filtered, washed up to neutral pH and dried at laboratory temperature. The shape of this amorphous substance can be seen in Fig. 1(c).

2.1.4. Potassium salt of 4,6-dinitrobenzofuroxan (KDNBF)

The potassium salt of 4,6-dinitrobenzofuroxan (KDNBF) was prepared according to the Spear and Norris procedure [9]. The

particle size and shape, documented by electron microscopy, are presented in Fig. 1(d).

2.1.5. Pure lead azide (LA)

Pure lead azide (LA) – the crystalline agent was not used during LA production – was provided by the Austin Detonator Company, Czech Republic. The particle size and shape, documented by electron microscopy, are presented in Fig. 1(e).

2.1.6. Dextrinated lead azide

Dextrinated lead azide (DLA) was provided by the Austin Detonator Company, Czech Republic. The crystal size and shape, documented by electron microscopy, are presented in Fig. 1(f).

2.1.7. Lead styphnate (LS)

Pure lead styphnate (lead salt of 2,4,6-trinitrobenzene-1,3-diol; LS) was provided by the Austin Detonator Company, Czech Republic. The crystal size and shape, documented by electron microscopy, are presented in Fig. 1(g).

2.1.8. Triacetone triperoxide (TATP)

Triacetone triperoxide (3,3,6,6,9,9-hexamethyl-1,2,4,5,7,8-hexaoxonane; TATP) was prepared by the standard route from acetone and hydrogen peroxide catalyzed by hydrochloric acid according to the procedure already published in our previous work (weight was one fifth of original procedure) [10]. The measuring of friction sensitivity was carried out the day after preparation. The crystal size and shape, documented by optical microscopy, are presented in Fig. 1(h).

2.1.9. Diacetone diperoxide (DADP)

Diacetone diperoxide (3,3,6,6-tetramethyl-1,2,4,5-tetraoxane; DADP) was prepared according to the Dubnikova procedure by transformation of TATP in the presence p-toluenesulfonic acid in a dichloromethane solution [11]. Raw DADP was purified by crystallization from methanol. The measuring of friction sensitivity was carried out the day after preparation. The crystal size and shape, documented by optical microscopy, are presented in Fig. 1(i).

2.1.10. Hexamethylenetriperoxide diamine (HMTD)

Hexamethylenetriperoxide diamine (3,4,8,9,12,13-hexaoxa-1,6-diazabicyclo[4,4,4]tetradecane; HMTD) was prepared according to the well known Girsewald procedure modified by Urbański [12]. The crystal size and shape, documented by electron microscopy, are presented in Fig. 1(j).

2.1.11. Tetrazene (GNGT)

Pure tetrazene (1-amino-1-(1H-tetrazol-5-yl) diazenyl) guanidine; GNGT) was provided by the company Sellier & Bellot a.s., Czech Republic. The crystal size and shape, documented by electron microscopy, are presented in Fig. 1(k).

2.1.12. Dinitrodiazophenol (DDNP)

Dinol (2-diazo-4,6-dinitrophenol; DDNP) was prepared according to the Garfield and Dreher procedure [13]. Only the catalyst (triphenylmethane dyes) was not used. The crystal size and shape, documented by electron microscopy, are presented in Fig. 1(l).

2.1.13. Brown mercury fulminate (brown MF)

The brown modification of mercury fulminate (MF) was prepared according to the usual procedure [8]. Mercury (5 g, 24.9 mmol) was dissolved in 30 ml (0.433 mol) of 65% nitric acid without agitation. Immediately after mercury dissolving this solution was poured into 45 ml (0.793 mol) of 96% ethanol. The vigorous reaction started within several minutes attended by evolution of

white fumes. The first mercury fulminate crystals formed on the bottom of reaction vessel after 10–15 min after mixing of both solutions. Reaction finished after about 45 min, the crystals of mercury fulminate were filtered, washed several times with water and finally with ethanol. The crystal size and shape, documented by optical microscopy, are presented in Fig. 1(m).

2.1.14. White mercury fulminate (white MF)

The procedure for preparing white mercury fulminate is similar to the procedure for brown mercury fulminate [14]. Mercury, (5 g, 24.9 mmol), 0.05 g powdered copper and 0.05 g 35% hydrochloric acid were dissolved in 30 ml (0.433 mol) 65% nitric acid without agitation. The rest of the process is the same as in the case of

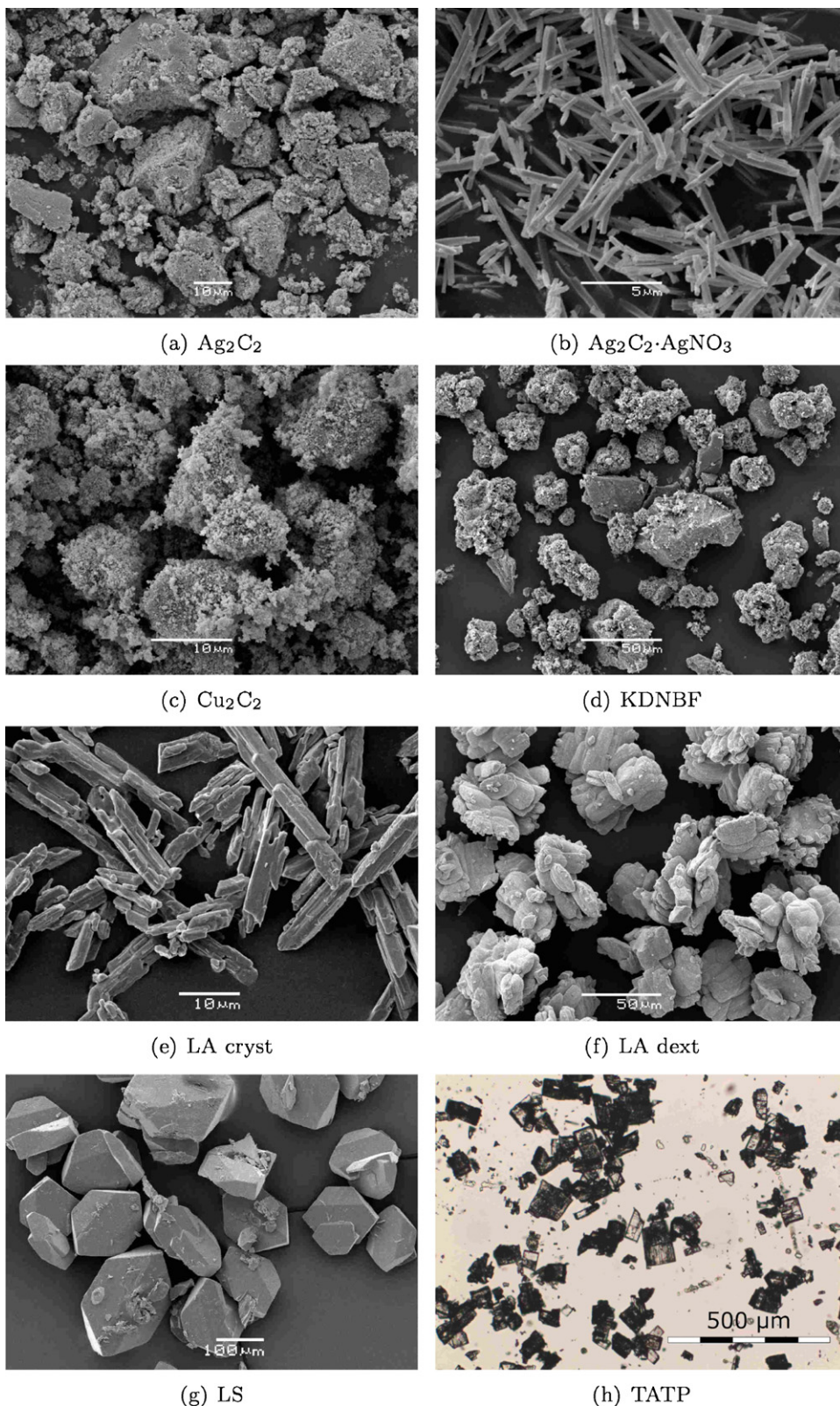
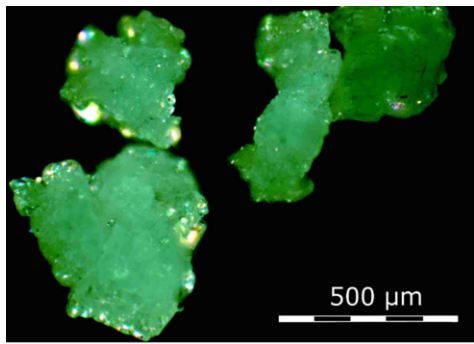
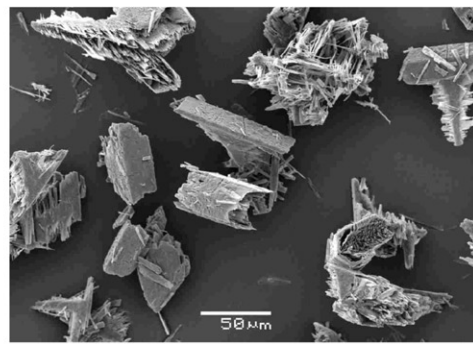


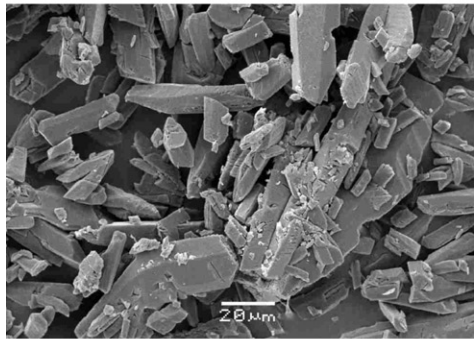
Fig. 1. The crystal shape and size of explored samples.



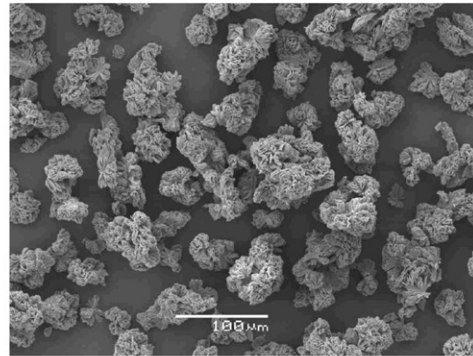
(i) DADP



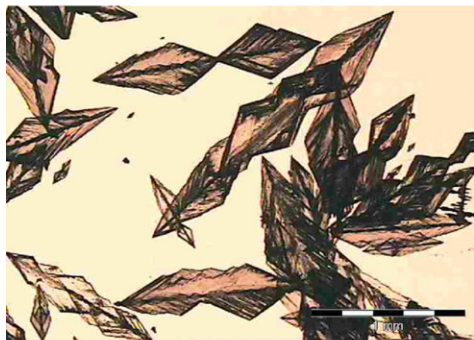
(j) HMTD



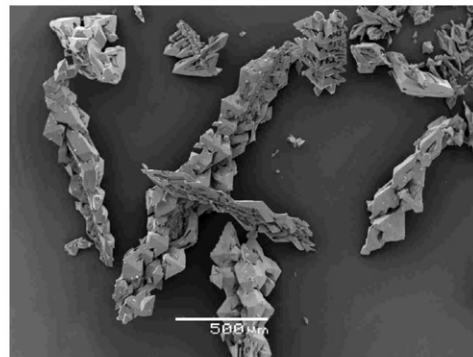
(k) GNGT



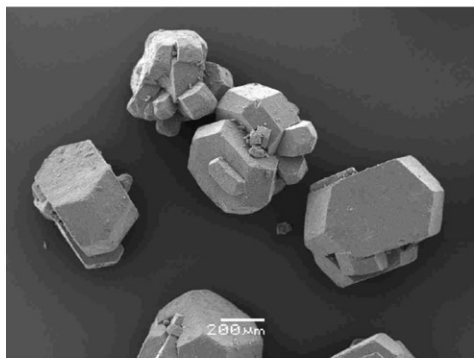
(l) DDNP



(m) brown MF



(n) white MF



(o) PETN D

Fig. 1. (Continued).

brown mercury fulminate. The crystal size and shape, documented by electron microscopy, are presented in Fig. 1(n).

2.2. Sensitivity measurement

The sensitivity to friction was determined using FSKM-PEx (OZM Research, Czech Republic) friction sensitivity tester. It is a modernized version of a standard BAM small-scale friction tester. The single side roughened ceramic plates (type BFST-Pt-100S) and porcelain pegs (type BFST-Pn-200) were provided by OZM Research, Czech Republic.

The samples were not specially dried before measuring. Potential presence of water in samples was checked by IR spectroscopy. The increased level of moisture was not observed in case of any sample. The relative humidity of the air was 40–55% during the measurements.

The probit analysis [15] was used to evaluate the friction sensitivity of all samples. The probit analysis was chosen because this method is suitable for producing the whole sensitivity curve, not only a single point of friction sensitivity.

The probability of ignition of each sample was determined using 4–7 levels of friction force, with 15 trials at each level. The probabilities obtained were expressed as probits and the linear regression between probits and logarithms of the friction force was performed. The sensitivity curve was obtained by backward transformation of the regression line into the probability–friction force coordinates.

The sensitivity of PETN was measured using the same method to serve as a reference for comparing with the sensitivities of primary explosives. PETN is one of the most sensitive secondary explosives and its sensitivity is sometimes used to distinguish between primary and secondary explosives. The sample of PETN D (pentaerythritol tetranitrate) was a standard industrial product from Explosia, a.s. company, Czech Republic. The crystal shape and the size of the crystals can be seen in Fig. 1(o).

3. Results and discussion

Preparation of primary explosives is described in the experimental section. Industrial primary explosives were either provided by industrial companies or synthesized by commonly used procedures. All improvised primary explosives were synthesized by procedures that are published in various modifications on web pages that deal with improvised explosives (e.g. Sciencemadness.org [16]).

The crystal size and shape of all measured primary explosives were documented by optical or electron microscope (Fig. 1).

The sensitivity curves obtained were split into two figures for more clarity. The more sensitive samples can be seen in Fig. 2 and

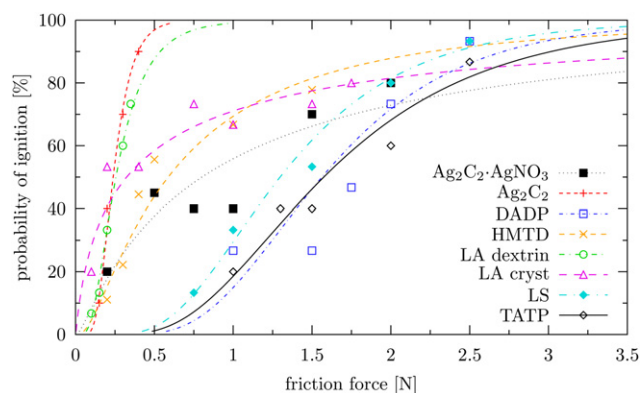


Fig. 2. The friction sensitivity curves of the more sensitive samples.

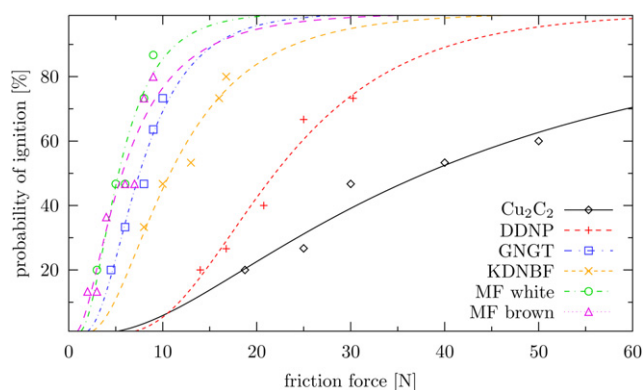


Fig. 3. The friction sensitivity curves of the less sensitive samples.

the less sensitive samples can be seen in Fig. 3. The following conclusions can be formulated:

- The tested samples can be divided into several groups, according to decreasing friction sensitivity:
 1. Ag_2C_2 and dextrinated LA;
 2. crystalline LA, HMTD and $\text{Ag}_2\text{C}_2 \cdot \text{AgNO}_3$ with more flat sensitivity curves;
 3. LS, DADP and TATP;
 4. both MFs, GNGT and KDNBF;
 5. and DDNP with Cu_2C_2 .
- The second most sensitive sample was lead azide. This primary explosive is well known and commercially produced. The manipulation with other primary explosives studied should be relatively safe, if one follows the safety precautions used in lead azide production.
- The organic peroxides (TATP, DADP and HMTD) are sometimes (e.g. [6]) reported as extremely sensitive substances. Our measurements do not confirm this suggestion – the friction sensitivity of organic peroxides is between that of lead azide and that of mercury fulminate.

The whole sensitivity range for the primary explosives tested covers two orders of magnitude (see Fig. 4), whereas in case of secondary explosives, this range is narrower. Between a typical sensitive secondary explosive (recrystallized PETN, $F_{50} = 64 \text{ N}$ [17]) and a typical insensitive secondary explosive (recrystallized TNT, $F_{50} > 360 \text{ N}$ [17]) the spread is about one order of magnitude.

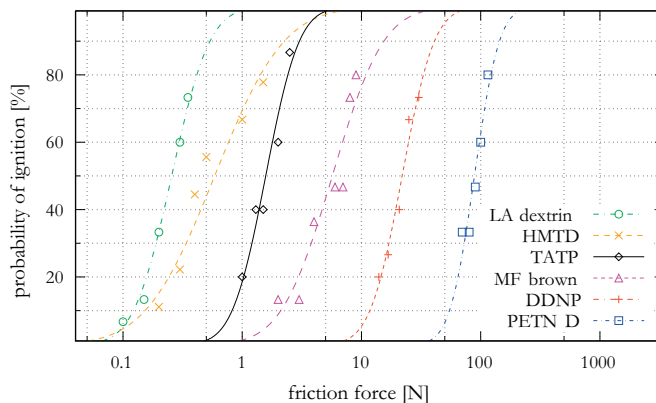


Fig. 4. The friction sensitivity range for primary explosives.

4. Conclusion

The sensitivity to friction was measured for 14 primary explosives. The sensitivity curves obtained represent a unique set of data, which cannot be found anywhere in the available literature. These samples were divided into five groups according to their sensitivity. Lead azide is one of the most sensitive samples and it is used in industrial applications. Therefore, it can be said, that manipulating the other samples studied should be relatively safe, if one follows the safety rules for lead azide production. Organic peroxides are not as extremely sensitive as it is sometimes stated, their sensitivity to friction being between that of lead azide and that of mercury fulminate.

Acknowledgements

This work was created as a part of the Ministry of Interior of the Czech Republic Project No. VG20102014032 and the Ministry of Education, Youth and Sports of the Czech Republic Project No. MSM 0021627501.

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